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TECHNICAL FIELD OF THE INVENTION

10 The present invention is directed towards malto-oligosaccharide derivatives, and towards methods for the preparation thereof. More specifically, the invention is directed in its preferred embodiments towards malto-oligosaccharides that have been derivatized by oxidation,
15 etherification, esterification, or enzymatic modification.

BACKGROUND OF THE INVENTION

20 Oligosaccharides are commonly prepared by the controlled hydrolytic cleavage of starches. In the production of such oligosaccharides, the glycosidic linkages of the starch molecules are partially hydrolyzed to yield at least one oligosaccharide species, and more
25 typically, a mixture of oligosaccharides species. Oligosaccharide mixtures so prepared typically include at least one malto-oligosaccharide species. Malto-oligosaccharides are characterized as having a saccharide backbone that comprises predominantly 1-4 glycoside
30 linkages.

 Malto-oligosaccharides comprise a commercially important class of carbohydrates that fall within the general class of reducing carbohydrates, which are carbohydrates that include an acetal group that is in
35 equilibrium with its respective aldehyde or ketone. Such malto-oligosaccharides find numerous commercial applications. Derivatized malto-oligosaccharides also are known in the art. Such derivatized malto-oligosaccharides also have many commercial uses,
40 including, for example, encapsulants, acidulants, flocculants, adhesives, antiredeposition agents, detergent builders, and so forth.

5 The prior art has provided numerous processes for
the derivatization of malto-oligosaccharides. Known
processes are conventional and typically comprise
derivatizing the malto-oligosaccharide via a conventional
derivatizing process to form a derivatized product. Such
10 prior art processes suffer from a number of drawbacks,
however. For example, when subjected to certain reaction
conditions, such as alkaline conditions, malto-
oligosaccharides can degrade and/or undergo numerous side
reactions to form respectively undesired products of
15 degradation or reaction by-products. Such by-products
and products of degradation lead to poor reaction yields,
undesired color formation, and difficulties in purifying
the desired derivatized malto-oligosaccharides.

It is believed that the so-called "alkaline peeling
20 reaction," in which the reducing end sugar of a malto-
oligosaccharide degrades into smaller molecules,
contributes substantially to degradation and by-product
formation in the derivatization of malto-
oligosaccharides. In recognition of this alkaline
25 peeling reaction, the prior art has taught in other
contexts to convert a base saccharide to a glycoside, to
thereby incorporate a protecting group. For example, it
is known to incorporate a methyl protecting group at the
reducing end of glucose to thereby form the alkaline-
30 stable methyl glycoside. Another approach used in the
prior art is the use of non-reducing sugars such as
sucrose and trehalose as protecting groups. For example,
U.S. Patent 5,780,620 (Mandai et al.) purports to
disclose non-reducing oligosaccharides wherein one or
35 several glucosyl groups are bound to both glucosyl groups
in trehalose. While the use of protecting groups such as
sucrose or trehalose in connection with the preparation
of a glycoside may afford an alkaline-stable product, the
process of preparing such stabilized malto-
40 oligosaccharides can be laborious and not economically
attractive.

5 It is a general object of the present invention to
provide a method for derivatizing a malto-
oligosaccharide. In accordance with preferred
embodiments of the invention, by-product formation and
formation of products of degradation are mitigated as
10 compared with products formed by known malto-
oligosaccharide derivatization reactions. It is also a
general object of the invention to provide a derivatized
malto-oligosaccharide product.

15

THE INVENTION

The invention is premised upon the surprising
discovery that reduced malto-oligosaccharides not only
are alkaline-stable with respect to unmodified malto-
20 oligosaccharides, but also may be derivatized to form
derivatized malto-oligosaccharides with a surprising
decrease in by-products and products of degradation, and
further providing other unexpected benefits, including
improved yields and improved ease of purification.
25 Further surprising in conjunction with the derivatization
of a mixture of malto-oligosaccharides is the discovery
that the change in DP profile of the mixture upon
oxidation, and, it is believed, other derivatization, is
smaller in conjunction with reduced malto-
30 oligosaccharides as compared with unmodified malto-
oligosaccharides. Thus, not only does the derivatization
of reduced malto-oligosaccharides generally result in
relatively less formation of by-products and products of
degradation, relatively increased yield, and ease of
35 purification with regards to unmodified malto-
oligosaccharides, the DP profile of the derivatized
malto-oligosaccharide mixture generally will be
relatively closer to that of the starting mixture.

In accordance with the invention, a method for
40 preparing a derivatized malto-oligosaccharide is
provided. Generally, the method comprises the steps of

5 providing a hydrogenated malto-oligosaccharide, and
derivatizing the hydrogenated malto-oligosaccharide to
thereby form a derivatized malto-oligosaccharide. The
malto-oligosaccharide may be obtained via the steps of
providing the malto-oligosaccharide and hydrogenating the
10 malto-oligosaccharide to thereby obtain a hydrogenated
malto-oligosaccharide. Derivatized malto-
oligosaccharides prepared in accordance with the method
of the invention also fall within the scope of the
invention. The scope of derivatization encompassed by
15 the invention is not contemplated to be limited, and
thus, for example, the hydrogenated malto-
oligosaccharides may be derivatized via oxidation,
esterification, etherification, or other suitable
derivatization reaction. The hydrogenated malto-
20 oligosaccharide also may be modified enzymatically to
yield enzymatically modified malto-oligosaccharides.

In a particularly preferred embodiment of the
invention, a mixture of hydrogenated malto-
oligosaccharide is derivatized. Most preferably, the
25 mixture is obtained via the hydrogenation of a mixture of
malto-oligosaccharides under reaction conditions suitable
to substantially preserve the DP profile of the reaction
mixture, as taught in co-pending application Serial No.
PCT/US99/01098.

30

DESCRIPTION OF PREFERRED EMBODIMENTS

The method of the invention is generally
contemplated to be applicable to any malto-
oligosaccharides species or mixture of a plurality of
35 malto-oligosaccharides species. By "malto-
oligosaccharide" is contemplated any species comprised of
plural saccharide units linked predominately via 1-4
linkages, thus including, for example, maltodextrins and
syrup solids. In preferred embodiments of the invention,
40 at least 50% of the saccharide units in the malto-
oligosaccharide are linked via 1-4 linkages. More

5 preferably, at least about 60% saccharide units are linked via 1-4 linkages; even more preferably, at least about 80% of the saccharide units are so linked. Malto-oligosaccharides are contemplated to include saccharides species having an odd DP value, such as maltotriose.

10 Malto-oligosaccharides may be characterized by their degree of polymerization (DP), which refers to the number of saccharide monomer units in each molecule. Each malto-oligosaccharide saccharide species also may be characterized by its dextrose equivalent value (DE),
15 which generally indicates the proportion of aldehyde, hemiacetal, or ketone groups in the molecule. Malto-oligosaccharides having a DE less than 20 prior to hydrogenation are known as maltodextrins, whereas malto-oligosaccharides having a DE of 20 or greater are known
20 as syrup solids. The invention is contemplated to find particular applicability in connection with the derivatization of mixtures of a plurality of malto-oligosaccharides species. The malto-oligosaccharides species in the mixture may be different at least in DP
25 value, thus defining a DP profile for the mixtures. The DP profile may be partially defined by a saccharides species having a DP value of 1, for example, dextrose or sorbitol. The mixture further may include other saccharides species or other components.

30 Preferably, in conjunction with the derivatization of a mixture of malto-oligosaccharides, at least a portion of the malto-oligosaccharides species in the mixture has a DP value greater than 5, and more preferably, at least one of the malto-oligosaccharides
35 species in the mixture has a DP value of 8 or more. More preferably, at least one species has a DP value of at least 10. For example, in preferred embodiments of the invention, at least 80% of the malto-oligosaccharides species in the mixture have a DP greater than 5, and at
40 least 60% may have a DP greater than 8. In another embodiment, at least 80% of the malto-oligosaccharides

5 species have a DP greater than 10. In some embodiments
of the invention, the DP profile of the malto-
oligosaccharides mixture is such that at least 75% of the
malto-oligosaccharides species in the mixture have a DP
greater than 5 and at least 40% species in the mixture
10 have a DP greater than 10. Such starting materials may
be obtained conventionally, for example, by the partial
hydrolysis of starch.

Suitable malto-oligosaccharides are sold as malto-
dextrins under the trademark MALTRIN® by Grain Processing
15 Corporation of Muscatine, Iowa. The MALTRIN® malto-
dextrins are malto-oligosaccharide products, each product
having a known typical DP profile. Suitable MALTRIN®
malto-dextrins that may be derivatized in accordance with
the present invention include, for example, MALTRIN®
20 M040, MALTRIN® M050, MALTRIN® M100, MALTRIN® M150, and
MALTRIN® M180. Typical approximate DP profiles for the
subject MALTRIN maltodextrins are set forth in the
following table (the DP profiles being approximate as
indicated in the table):

Typical DP profile (% dry solids basis)					
DP profile	M180	M150	M100	M050	M040
DP>8	46.6 +4%	54.7 +4%	67.8 +4%	90.6 +4%	88.5 +4%
DP 8	3.9 +2%	4.8 +1.5%	4.5 +1.5%	1.5 +1%	2.0 +1%
DP 7	9.5 +2%	9.1 +1.5%	7.0 +1.5%	1.5 +1%	2.4 +1%
DP 6	11.4 +2%	8.4 +1.5%	6.1 +1.5%	1.4 +1%	1.8 +1%
DP 5	5.9 +2%	4.7 +1.5%	3.3 +1.5%	1.3 +1%	1.3 +1%
DP 4	6.4 +2%	5.5 +1.5%	3.7 +1.5%	1.1 +1%	1.4 +1%
DP 3	8.3 +2%	6.7 +1.5%	4.2 +1.5%	1.0 +1%	1.4 +1%
DP 2	6.2 +2%	4.8 +1%	2.5 +1%	0.8* +1%	0.9* +1%
DP 1	1.8 +1.5%	1.3 +1%	0.7* +1%	0.8* +1%	0.3* +1%

* MINIMUM VALUE = 0%

The invention encompasses the derivatization of maltodextrin starting materials that have substantially the foregoing approximate DP profiles, however made. Other malto-oligosaccharides suitable for use in conjunction with the invention include other malto-dextrins, such as MALTRIN® M440, MALTRIN® M510, MALTRIN® M550, MALTRIN® M580, MALTRIN® M700, as well as corn syrup solids such as MALTRIN® M200 and MALTRIN® M250 (these having a DE > 25 prior to hydrogenation). The invention is not limited to derivatization of the foregoing malto-oligosaccharides species or mixtures, and indeed, any suitable malto-oligosaccharide may be derivatized in conjunction with the invention.

Most preferably, the mixture of malto-oligosaccharides is catalytically hydrogenated to thereby substantially reduce the malto-oligosaccharides in the mixture, in some cases to a DE of essentially zero, as set forth in more detail in co-pending application serial no. PCT/US98/01098 (published as WO 99/36442). By "substantially reduced" is meant that the DE of the malto-oligosaccharide is reduced by at least about 85%, and preferably at least about 90%, relative to the initial DE thereof. The term "essentially zero" as used herein with respect to DE value refers to hydrogenated product having a DE of less than about 1. Further details concerning catalytic hydrogenation of malto-oligosaccharide mixtures are set forth in the aforementioned co-pending application serial no. PCT/US98/01098.

While is not intended to limit the invention to a particular theory of operation, it is believed that the reducing end group at the leading C-1 position of the malto-oligosaccharide aldose is generally the most reactive group on the molecule. When an unmodified malto-oligosaccharide is derivatized, for example, by oxidation, it is believed that oxidation will occur first

5 at this position, followed by oxidation at the primary
alcohol (C-6) positions on the molecule. Because the
rate of the reaction is higher at the C-1 reducing end
group, alternative degradation mechanisms may occur by
the time the C-6 alcohols are oxidized. When the
10 reducing end group is hydrogenated to form the
corresponding alditol, however, this phenomenon is
mitigated against. All of the primary alcohol groups on
the malto-oligosaccharides molecule will oxidize at
similar rates, thus limiting the amount of by-product
15 formation. As the degree of polymerization of the malto-
oligosaccharides increases, the number of C-6 groups
increases relative to the single leading C-1 group on the
malto-oligosaccharide molecule, thus leading to
proportionally greater benefits.

20 In accordance with the invention, the malto-
oligosaccharide is derivatized, by which generally is
contemplated incorporating one or more substituents or
chemical modifications in one or more positions on one or
more saccharide units in the malto-oligosaccharide
25 molecule. The extent of the derivatization can be
expressed via the degree of substitution (DS) of the
malto-oligosaccharide. In conjunction with the
invention, it is possible to derivatize the malto-
oligosaccharide to a DS of greater than or equal to 0.25,
30 even more preferably, a DS of about 0.5 and even more
preferably, a DS greater than about 0.8. Where
applicable, the extent of derivatization may be expressed
in terms of molar substitution ("MS"), for example, in
the case of hydroxyalkylation. The extent of
35 derivatization may be adjusted to the degree desired for
a given application. Surprisingly, it has been found
that the use of hydrogenated malto-oligosaccharides often
affords a product that has a higher DS than that which
would be obtained via derivatization of an unmodified
40 malto-oligosaccharide under similar reaction conditions.
The invention is applicable to the derivatization of

5 mixtures of malto-oligosaccharides, wherein at least a
portion of the malto-oligosaccharides in the mixture are
derivatized. By "at least a portion" is contemplated any
portion of the malto-oligosaccharides, including without
10 limitation the derivatization of some or all malto-
oligosaccharides of a given DP value.

While the invention is applicable to any
derivatization via any substituent, the invention finds
particular applicability to those derivatization
chemistries that employ alkaline conditions.
15 Particularly suitable derivatizations include oxidations,
etherifications, and esterifications. The invention is
also applicable to enzymatic modifications of the malto-
oligosaccharide, which enzymatic modifications may result
in an oxidized, etherified, esterified or otherwise
20 derivatized or modified malto-oligosaccharide.
Generally, any reaction conditions that will result in a
derivatized malto-oligosaccharide, except possibly highly
acidic conditions that might allow for hydrolysis of
glycosidic linkages, may be employed. The malto-
25 oligosaccharide preferably is derivatized in aqueous
solution at a pH greater than about 6.0, and more
preferably under alkaline conditions (i.e., a pH greater
than 7.0).

For example, with respect to derivatization the
30 oxidation of the malto-oligosaccharide in one or more
primary alcohol positions to form carboxylic acids, a
variety of oxidation reactions are known in the art and
are applicable for use in conjunction with the invention.
Suitable oxidizing reactants include nitroxyl radicals,
35 nitrogen dioxide and tetroxide, and hydrogen peroxide.
Alternatively, the oxidation may also be effectuated
enzymatically or via electrolytic methods. Suitable such
reactions are disclosed in Arts et al., Synthesis 1997
(6): 597-613; Roper, in Carbohydrates As Organic Raw
40 Materials, Ch. 13: 267-288 (1991); and in published
International Application No. WO 95/07303.

5 In accordance with a preferred embodiment of the invention, the malto-oligosaccharide is oxidized in the presence of a metal catalyst, such as platinum or palladium. The oxidation of glucose using palladium on carbon doped with bismuth has been described in EP
10 142,725 and in U.S. Patent No. 4,845,208, and the oxidation of starch hydrolysates has been disclosed in U.S. Patent 4,985,553 and in published International Application No. WO 97/34861. Platinum is preferred over palladium for oxidizing alcohol groups, inasmuch as
15 platinum is less prone to deactivation by oxygen. However, platinum-catalyzed oxidation of dextrose to yield glucaric acid traditionally has been plagued with high levels of by-product formation. In EP 775,709, a method of combining noble metal catalysis with an
20 electrodialysis separation is disclosed. Other oxidations known in the art include those disclosed in Glattfeld and Gershon, J. Am. Chem. Soc. 60:2013 (1938); Heynes and Paulsen, Ang. Chem. 69:600 (1957); Heynes and Beck, Chem. Ber. 91:1720 (1958); U.S. Patent 5,109,128;
25 EP 548,339. WO 95/07303 (use of 2,2,6,6,-tetramethylpiperdine 1-oxyl in conjunction with an oxidant system that includes sodium bromide and sodium hypochlorite to oxidize carbohydrates selectively at the C-6 position at pH's ranging from 9.8 to 11.5), and WO
30 92/18542 (alkaline oxidation in the presence of metal ions in molecular oxygen, and a polydentate and amine ligand).

The invention also is contemplated to be applicable to etherification of malto-oligosaccharides. Preferred etherification reactions include ethoxylations,
35 propoxylations, and similar alkoxylation, as well as reactions to introduce a cationic charge by using reagents such as 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride or like reagents. Any suitable reagents in reaction conditions as are known or as may be
40 found to be suitable may be used in conjunction with the invention. For example, reagents such as octyl bromide,

5 allyl bromide, propylene oxide, ethylene oxide, and like
chemicals conventionally used in connection with ether
formation may be employed, as well as higher molecular
weight polymers conventionally used in epoxide ring
opening or nucleophilic displacement reactions, such as
10 glycidyl ethers, and so forth. The etherification
reaction may comprise combining the malto-oligosaccharide
and alkylene oxide in any amount effective to achieve
derivatization. In one embodiment, the alkylene oxide is
present in an amount greater than 40% by weight of the
15 malto-oligosaccharides starting material, such as an
amount greater than 45% by weight of the malto-
oligosaccharide starting material. The reaction
conditions may be any conditions suitable to form a
malto-oligosaccharide-alkyl ether.

20 Another example of the derivatization of a malto-
oligosaccharide is via esterification. The
esterification reaction preferably incorporates any acyl
group having from 2 to 20 carbon atoms. The acyl group
may be added via conventional means, such as using an
25 acid chloride or acid anhydride, or by such other means
as may be found to be suitable. The malto-
oligosaccharide may be esterified to form an acetate,
benzoate, octenylsuccinate, or other suitable ester. A
common esterification reaction in which a hydrogenated
30 malto-oligosaccharide would be advantageous is an
octenyl-succinylation reaction, such as that disclosed in
U.S. Patent 5,720,978.

The malto-oligosaccharide also may be derivatized
via enzymatic modification. Any suitable enzyme as may
35 be known or may be found to be suitable may be used in
conjunction with the invention to modify the malto-
oligosaccharide. It is contemplated that the enzymatic
modification may result in a malto-oligosaccharide that
is oxidized, esterified, or otherwise derivatized or
40 modified. The term "derivatized" in conjunction with an
enzymatically modified malto-oligosaccharide is intended

5 to encompass such modifications as may be effected by the enzymatic modification.

The following non-limiting Examples are provided to illustrate preferred embodiments of the present invention.

10

EXAMPLES

Example 1

Oxidation of Malto-Oligosaccharide

In 651 ml of deionized water was slurried 1.79 grams
15 10% platinum on graphite (Johnson Matthey type B101026-10). The slurry was heated to 60° C while purging with nitrogen (1.5 L/min). Once the slurry reached temperature, 14.7 grams hydrogenated MALTRIN® M180 was added. The nitrogen flow was replaced with 0.2 L/min
20 oxygen. The reaction pH was controlled at pH 9.0 with 0.5M NaOH. Once 0.25 equivalents of NaOH was consumed (5 hours), the oxygen flow was terminated and the sample was diluted to 2 liters, then vacuum filtered through #3 Whatman filter paper, frozen, and freeze dried. The
25 samples were analyzed for ash and for carboxyl degree of substitution via a conventional titrametric process. MALDI (matrix-assisted laser desorption ionization) mass spectra was obtained.

- 5 As a control, 14.8 grams unmodified MALTRIN® M180 was oxidized under similar reaction conditions. After 5 hours and 49 minutes, 0.127 equivalents of NaOH was found to have been consumed. The following results were obtained:

10

Analysis	Example 1	Control
Ash	2.18	6.83
DS	0.206	0.322

Degree of Polymerization (DP)	Sample Molecular Weight				
Units	MALTRIN® M180	Example 1 (Derivatized Hydrogenated MALTRIN® M180)		Control (Derivatized MALTRIN® M180)	
		Major Peak	Minor Peak	Major Peak	Minor Peak
3	530	565	545	527	549
4	690	727	692	689	728
5	851	890	853	851	891
6	1013	1052	1014	1013	1052
7	1175	1214	1176	1175	1214
8	1337	1376	1337	1339	--
9	1498	1499	1538	1501	--
10	1660	1660	1700	1662	--
12	1985	1984	2021	1988	--
14	2308	2308	2346	2310	--
16	2632	2630	2669	2632	--
18	2955	2954	2992	2954	--
20	3281	3277	--	3276	--
26	4244	4241	--	--	--
41	6678	--	--	--	--

5 The degree of substitution was higher for the control because the uncontrolled oxidation reaction created more carboxyl groups as degradation products.

10 The color of the product of Example 1 was significantly less than that of the control. The mass spectra indicated a significant drop in the overall molecular weight and DP profile of both of the oxidized samples, but a significantly greater preservation of molecular weight with the product of Example 1, with the maximum observed peak given as 4241 daltons for example 15 1, and 3276 daltons for the control.

Example 2

Propoxylation of Malto-Oligosaccharide

20 In a 500 ml reaction flask, which was equipped with a magnetic stirrer, a temperature control, and a condenser, 200 grams hydrogenated maltodextrin (MALTRIN® M180) was dissolved in 60 grams deionized water. To this solution was added 5.6 grams potassium hydroxide and 62.8 25 grams propylene oxide. The reaction mixture was refluxed for 16 hours, and allowed to heat to 65° C. Once the reaction reached temperature, it was terminated with the addition of 7 grams sodium bisulfite. The final reaction mixture had an orange color. The reaction mixture was 30 ion-exchanged on a dual column system of 150 ml DOWEX® MONOSPHERE 66 (hydroxide form) and 150 ml DOWEX® MONOSPHERE 88 (hydrogen form), and then freeze dried to give a white product.

35 As a control, 140 grams MALTRIN® M180 was similarly propoxylated. The reaction mixture was a dark orange to brown color after termination with sodium bisulfite. After ion exchanging and freeze drying, the given product had a yellow color.

5 Each product was evaluated for hydroxypropyl degree of substitution via a conventional technique. The following results were obtained:

Analysis	Example 2	Control 2
DS	0.93	.46

10 The color of the control was significantly greater than the product of Example 2. No significant difference in maximum molecular weight was observed. The propoxylation reaction of the present invention thus yielded a product having significantly less color and higher DS as compared
15 with the control.

Example 3

Carboxymethylation of Malto-Oligosaccharide

20 Fifty grams of hydrogenated MALTRIN® M100 was dissolved in 100 ml water. Monochloroacetic acid (0.5 equivalents) was added, followed by 24.2 grams of 50% NaOH (1.0 equivalent). The mixture was heated to 70° C. and held at this temperature for 2 hours. After 2 hours,
25 the pH was measured and found to be 11.2, after which the pH was adjusted to a final pH of 8.0 with the addition of 6N HCl. The reaction contents were cooled and then slowly poured into 2000 liters methanol to precipitate a beige-colored solid. The solid was washed with a second
30 200 ml aliquot of methanol and dried under vacuum for 2 days to yield 58.1 grams of a product which contained 13.4% moisture and 5.75 ash. The ash-moisture-corrected theoretical yield of the product was 85%. The DS was determined via a conventional titrametric process and was
35 found to be 0.30. MALDI molecular weight analysis demonstrated a maximum molecular weight of 2241 daltons and strong evidence of mono-, di- and tri-substituted carboxymethylation of the malto-oligosaccharide molecules.

5 As a control, 50 grams of MALTRIN® M100 was
carboxymethylated in a similar reaction. After the
initial reaction mixture had been held for 2 hours, the
reaction pH was found to be 8.0. The precipitated solid
was dark yellow, and the dry solid yield was 35.3 grams
10 product which contained 11.2 percent moisture and 4% ash.
The ash-and moisture-corrected theoretical yield was 54%,
and the DS was found to be 0.22. The maximum molecular
weight was found to be 1236 daltons, and the mass spectra
analysis gave some evidence only for mono-substitution.
15 The control had significantly more color than the product
of Example 3. This Example illustrates that a higher DS,
better recovery, better preservation of molecular weight,
and better color were obtained with hydrogenated malto-
oligosaccharides in accordance with the invention than
20 the control.

Example 4

Hydroxypropyl Trimethylammonium chloride Derivatization of Malto-Oligosaccharide

25 Two hundred grams (dry solid basis) of hydrogenated
MALTRIN® M100 was dissolved in 280 ml water. To this
solution was added 24.0 grams of a 50% solution (0.24
equivalents) sodium hydroxide over a period of 10
30 minutes. QUAB 151 (2,3 epoxypopyl-n,n,-
trimethylammonium chloride, DeGussa Corp.) 214.0 grams of
a 70% solution (0.8 equivalents) was added to the
reaction and the temperature was maintained at 60° C for
three hours. After three hours the reaction mixture was
35 a rusty brown color. The solution was pH-adjusted to 6.0
with HCl and freeze dried to yield 340 grams of a light
brown solid. The unpurified, recovered yield after
moisture and ash correction was 88%. MALDI molecular
weight analysis indicated a maximum molecular weight
40 about 1603 daltons.

As a control, 200 grams unmodified MALTRIN® M100 was
similarly derivatized. After three hours, the reaction

5 mixture was found to be black and viscous. The purified,
recovered yield was 92%, but MALDI molecular weight
analysis indicated a maximum molecular weight of about
1330 daltons. The control had significantly more color
than the Example. Both the products of Example 1 and of
10 the control were substituted to about the same extent, as
evidenced by nitrogen combustion analysis. Thus, the
Example provided a product with less color, and better
preservation of molecular weight than the control.

All of the foregoing examples illustrate that an
15 improved product, with improved ease of purification (as
evidenced by the lower color levels), may be obtained
using hydrogenated malto-oligosaccharides.

20 Example 5
Enzymatic Modification of Malto-Oligosaccharide

Hydrogenated MALTRIN® M180, 50g, is dissolved in 25g
of water and pH controlled at 7.0. Vinyl acetate, 5g, is
25 poured into the reaction mixture and the system stirred
vigorously. Porcine pancreatic lipase, 5g, is added and
the reaction is stirred for 24 hours at ambient
temperature. The resulting maltodextrin is isolated by
precipitation by ethanol, and dried to yield a partially
30 acetylated product.

While particular embodiments of the invention have
been shown, it should be understood that the invention is
35 not limited thereto since modifications may be made by
those skilled in the art, particularly in light of the
foregoing teachings. It is, therefore, contemplated by
the appended claims to cover any such modifications as
incorporate those features which constitute the essential
40 features of these improvements within the true spirit and
scope of the invention. All references and cited herein
are hereby incorporated by reference in their entireties.
The disclosure of co-pending application serial no.

5 PCT/US98/01098 also is hereby incorporated by reference
in its entirety.